FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 4006-007-30

U S APPLICATION NO. (IF KNOWN, SEE 37 CFR): 10/070918

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/BE98/00180	20 NOVEMBER 1998	20 NOVEMBER 1997

TITLE OF INVENTION

PROCESS AND PLANT FOR SEPARATING THE CONSTITUENTS OF WORN TYRES

APPLICANT(S) FOR DO/EO/US

DEBAILLEUL, Gerard

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☒ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Copy of the international application as published (WO 99/27004)
English translation of the International Preliminary Examination Report
Change of Address

U.S. APPLICATION NO (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/070918	PCT/BE98/00180	4006-007-30

24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**	
☒	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**	
☐	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**	
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**	
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**	
	ENTER APPROPRIATE BASIC FEE AMOUNT =	**$890.00**
	Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	15 - 20 =	0	x $18.00	**$0.00**	
Independent claims	1 - 3 =	0	x $84.00	**$0.00**	
Multiple Dependent Claims **(check if applicable).**			☐	**$0.00**	
	TOTAL OF ABOVE CALCULATIONS =			**$890.00**	
☒	Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.			**$445.00**	
	SUBTOTAL =			**$445.00**	
	Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +			**$0.00**	
	TOTAL NATIONAL FEE =			**$445.00**	
☐	Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).**			**$0.00**	
	TOTAL FEES ENCLOSED =			**$445.00**	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of **$445.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **50-1442** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Supervisor, Patent Prosecution Services
PIPER MARBURY RUDNICK & WOLFE, LLP
1200 Nineteenth Street, NW
Washington, DC 20036-2412
US

Jerold I. Schneider

SIGNATURE

SCHNEIDER, Jerold I.

NAME

24,765

REGISTRATION NUMBER

13 MARCH 2002

DATE

DOCKET NO. 4006-007-30

PATENT COOPERATION TREATY (PCT)

IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

In re Application of:	DEBAILLEUL, Gérard
Int'l Application No.:	PCT/BE98/00180
Int'l Filing Date:	20 NOVEMBER 1998
Priority Date:	20 NOVEMBER 1997
U.S. Application No.:	10/070,918
For:	PROCESS AND PLANT FOR SEPARATING THE CONSTITUENTS OF WORN TYRES

SUBSTITUTE
PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

SIR:

Please disregard the preliminary amendment filed March 13, 2002 in the above-identified application. This amendment replaces that earlier filed preliminary amendment. Prior to any examination on the merits, and with reference to the accompanying English translation, please amend this application as follows:

IN THE SPECIFICATION

Page 1, before the first paragraph and below the Title, insert the following section, including a section heading:

- - CROSS REFERENCE TO RELATED APPLICATIONS

This application is the U.S. National Stage of International Application No. PCT/BE98/00180 filed 20 November 1998, and Belgian Application No. 9700933

filed 20 November 1997. The entirety of each of those applications is incorporated herein by reference.

BACKGROUND OF THE INVENTION - -.

Delete the first paragraph, at page 1, lines 3-8, and insert therefor the following:

--The present invention relates to a process and a plant for the treatment of vulcanized rubber of all kinds, such as tyres, conveyor belts, boots, shoes and other objects containing assembled rubber and polymer materials for the purpose of recycling the components by the relevant industries.--.

Delete the fourth paragraph at page 2, lines 25-32, and insert therefor the following:

--GB 2,026,144 (1979) discloses a plant for the treatment of rubber waste and of synthetic materials coming from worn tyres. Thermal decomposition of the product, which is coarsely reduced, is carried out in a fluidized bed of sand at 800°C in the presence of oxygen. The gases produced by the decomposition are used and, at the end of the process, the reinforcing metals are recovered by means of magnets.--.

Page 3, between lines 18 and 19, insert the following section heading:

--SUMMARY OF THE INVENTION--.

Delete the first full paragraph, at page 4, lines 5-9, and insert therefor the following:

--B) The reduced waste is introduced into a reactor and treated for 30 minutes at 350°C with an OH^- ion generator, preferably a strong alkaline base such as molten NaOH. 3. Separation of the basic liquid and the residues coming from the treated rubber.--.

Page 4, between lines 32 and 33, insert the following section heading:

- - BRIEF DESCRIPTION OF THE DRAWINGS --.

Page 5, between lines 7 and 8, insert the following section heading:

- - DETAILED DESCRIPTION --.

Delete the first full paragraph at page 5, lines 8-27, and insert therefor the following:

--As shown in Figure 1, crystallized NaOH in its original package is melted in the oven 1, at a temperature of 300 to 400°C, before being introduced into the master tank 5, which is provided with a heater and in which the NaOH is maintained at a temperature of 380° before being transferred to the reactor 13 into which the waste coming from the cropper 14 is also introduced. After 30 minutes of immersion and with stirring at the start of obtaining a temperature of 350°C, the liquid is conducted by the line 19, provided with a pump, to the buffer tank 20 and then sent to the master tank 5. The buffer tank is heated to a temperature of 380°C in order to prevent heat shocks occurring in the tank 5. Moreover, the buffer tank is designed to gather the precipitates and is organized for the separation and extraction of the small particles. The decomposition products from the reactor 13 are transferred to the neutralization tank 23 and, at the end of the treatment, the residues are transported to the magnetic sorting device 32 where the metals are separated from the polymers resulting from the treatment.--.

Delete the second and third full paragraphs at page 6, lines 5-31, and insert therefor, the following:

--The master tank 5 is equipped with conventional monitoring and control instruments 8 to 11, known to those skilled in the art, which monitor the conditions in the tank and actuate the electronic control actuators when transfers are made and when other actions are taken. The regulatory safety valve 7 prevents unexpected and accidental overpressures and the heating element 6 (which may be placed on the

outside, between the insulation, by heating coils conveying a warm liquid) keeps the temperature constant inside the tank.

The liquid is sent via the line 12, fitted with a pump, into the reactor 13 and the waste, cut up in the cropper 14, advantageously a guillotine, is sent by the chain conveyor 15 into the reactor 13, the solid materials must be immersed, the amount of caustic liquid is attained by the operation and control of a probe which also actuates the closure of the valve 17 and the start of the stirring provided by the mixer 16. The temperature of the reactor is maintained by the heating system 18. After approximately 30 minutes treatment at 350°C, the materials are deconsolidated, the caustic liquid is extracted by the line 19, fitted with a pump, through a filter 21, to the buffer tank 20. The filter 21 retains the particles greater than 1 mm. It is unclogged suddenly by closing the valve of the line 19 and sending compressed air 44 into that part of the line 19 which is connected to the tank 13.--.

Delete the third paragraph, at page 8, line 15 - page 9, line 4, and insert therefor the following:

--As this is a heat treatment, it is preferable to work continuously as long as possible. For this purpose, and in order to avoid shut downs due to the build-up of impurities and small particles, cleaning devices are provided for removing them, without having to stop the production. After a number of treatments and in anticipation of cleaning the buffer tank 20, the NaOH liquid in the master tank 5 will be taken to the minimum level in order to receive the entire solution stored in the buffer tank 20, up to the level of the tap on the line 21. Next, water will be slowly added via the line 37 to the rest of NaOH liquid, bottom of the buffer tank 20 for a direct dilution to the point of non-crystallization (concentration +/- 40%). After this dilution, the valve 38 is opened on a vibrating screen 39 having a porosity of 10

microns. The solid particles are removed to a container 40 and will be able to be transferred thereafter to a washing tank external to the system with a filter press for the impurities precipitated by the neutralization and for recovering the materials to be recycled in a container of the 36 type. The 40% NaOH solution is recovered via the outlet 41. It will be put into drums and sold for another use or else introduced into the tank 24 in order to obtain a neutralizing agent and thus increase the profitability of the process.--.

Delete the third full paragraph, at page 9, lines 20-27, and insert therefor the following:

--During temporary shut-down or shut-down of short duration of the plant, the heating of the master tank 5 and possibly buffer tank must not be cut off. For a complete shut-down, it will be essential to drain, while hot, the buffer tank 20 to the master tank 5 and then via the line 43, connected to a battery of drums in which the solution will crystallize. To reuse the NaOH, the drums will be placed in the oven 1.--.

IN THE CLAIMS

Please cancel Claims 1 - 16 without prejudice or disclaimer, and add the following new Claims 17 - 31.

--17. (new) Process for treating vulcanized rubber waste, particularly tyres of all sizes and of all types and/or of other worn reinforced-rubber articles, such as boots, inflatable boats, this process comprising:

- coarse cutting of the said waste into fragments, and
- attacking said fragments using a molten pure base,

characterized in that said attacking of the fragments is carried out under temperature

conditions causing, in the presence of said attacking base, deconsolidation of the vulcanized rubber waste into deconsolidated solid fragments,
and in that the process furthermore comprises

- separating said molten base from said deconsolidated solid fragments,
- neutralizing the deconsolidated solid fragments, and
- recycling or reutilizing the neutralized, deconsolidated solid fragments.

18. (new) Process according to Claim 17, characterized by the use of molten pure cast NaOH as the attacking liquid.

19. (new) Process according to Claim 17, characterized in that said separation comprises sedimentation of the deconsolidated fragments, separated beforehand from the molten base, in a settling and neutralizing liquid, and, after removal of the settling and neutralizing liquid, recovery of the deconsolidated fragments.

20. (new) Process according to Claim 17, characterized in that it comprises a recycling of the molten pure base.

21. (new) Process according to Claim 18, characterized in that the molten NaOH treatment temperature is at most 400°C, advantageously at most 350°C.

22. (new) Process according to Claim 17, characterized in that the deconsolidated solid fragments comprise metal fragments and fragments made of synthetic material and in that the process furthermore includes sorting between the metallic and synthetic deconsolidated fragments before they are recycled or reutilized.

23. (new) Process according to Claim 17, characterized in that the deconsolidation treatment takes place in a closed reactor, the materials to be treated completely immersed.

24. (new) Process according to Claim 17, characterized in that the neutralization uses dilute acids, preferably phosphoric acid, more advantageously waste from certain phosphoric acid solutions.

25. (new) Plant for implementing the process for treating vulcanized-rubber waste according to Claim 17, characterized in that it forms a completely closed system, with no atmospheric pollution, which comprises:

- a device for melting said pure base;
- a reactor into which said vulcanized-rubber waste, coarsely cut into pieces, and said molten pure base as attacking medium are introduced, and in which reactor temperature conditions are applied causing deconsolidation of the vulcanized-rubber waste into solid fragments deconsolidated under the action of the attacking medium;
- a separating device allowing the molten base serving as the attacking medium to be separated from the deconsolidated solid fragments;
- a neutralizing device fed with neutralizing agent from a source of neutralizing agent, in which device the deconsolidated solid fragments are neutralized; and
- a device for sorting the neutralized, deconsolidated solid fragments.

26. (new) Plant according to Claim 25, characterized in that the reactor has closeable inlet and outlet openings, stirring equipment, and in that said separating device comprises a filter if necessary unclogged by a compressed-air device capable of retaining inside the reactor particles greater than 1 mm.

27. (new) Plant according to Claim 25, characterized in that the neutralizing device comprises a tank provided with an inlet communicating with the outlet of the reactor, and with an outlet, the inlet and outlet being closeable, stirring equipment and a filter if necessary unclogged by the compressed-air device in the output line with extension, spraying equipment for facilititating the neutralization via a line.

28. (new) Plant according to Claim 25, characterized in that the neutralizing device comprises a tank for injection of neutralized liquid and for recovery.

29. (new) Plant according to Claim 25, characterized in that the neutralizing device comprises another tank which contains acid waste and is connected to a mixing unit in the line.

30. (new) Plant according to Claim 25, characterized in that it comprises devices for cleaning the precipitates and small particles, during treatment.

31. (new) Plant according to Claim 25, characterized in that the sorting device comprises a device for transporting the deconsolidated materials with magnetic separation of the metallic materials, possibly combined with an eddy-current system for the non-ferrous materials.

REMARKS

This is the entry into the U.S. National Stage of International Application No. PCT/BE98/00180 filed 20 November 1998. The foregoing amendments place the specification into U.S. format and present Claims 17 - 31 for examination.

Applicant respectfully submits that, in view of the foregoing amendments and remarks, the application is in condition for examination. Favorable consideration is respectfully requested.

Respectfully submitted,

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SERIAL NO. 10/070,918

DOCKET NO.: 4006-007-30

MARKED-UP COPY OF PARAGRAPHS, AS AMENDED

Replacement for the first paragraph, at page 1, lines 3-9:

--The present invention relates to a process and a plant for the treatment of vulcanized rubber of all kinds, such as tyres, conveyor belts, boots, shoes and other objects containing assembled rubber and polymer materials for the purpose of recycling the [component [sic]] components by the relevant industries.--

Replacement for the fourth paragraph, at page 2, lines 25-32:

--GB 2,026,144 (1979) [of] discloses writing [[sic]] a plant for the treatment of rubber waste and of synthetic materials coming from worn tyres. Thermal decomposition of the product, which is coarsely reduced, is carried out in a fluidized bed of sand at 800°C in the presence of oxygen. The gases produced by the decomposition are used and, at the end of the process, the reinforcing metals are recovered by means of magnets.--

Replacement for the first full paragraph at page 4, lines 5-9:

--B) The reduced waste is introduced into a reactor and treated for 30 minutes at 350°C with an OH^- ion generator, preferably a strong alkaline base such as molten NaOH. 3. [[sic]] Separation of the basic liquid and the residues coming from the treated rubber.--;

Replacement for the first full paragraph at page 5, lines 8-27:

--As shown in Figure 1, crystallized NaOH in its original package is melted in the oven 1, at a temperature of 300 to 400°C, before being introduced into the master tank 5, which is provided with a heater and in which the NaOH is maintained at a temperature of 380° before being transferred to the reactor 13 into which the waste coming from the cropper 14 is also

introduced. After 30 minutes of immersion and with stirring at the start of obtaining a temperature of 350°C, [[sic]. The] the liquid is conducted by the line 19, [furnishes of [sic]] provided with a pump, to the buffer tank 20 and then sent to the master tank 5. The buffer tank is heated to a temperature of 380°C in order to prevent heat shocks occurring in the tank 5. Moreover, the buffer tank is designed to gather the precipitates and is organized for the separation and extraction of the small particles. The decomposition products from the reactor 13 are transferred to the neutralization tank 23 and, at the end of the treatment, the residues are transported to the magnetic sorting device 32 where the metals are separated from the polymers resulting from the treatment.--.

Replacement for second and third full paragraphs at page 6, lines 5-31:

--The master tank 5 is equipped with conventional monitoring and control instruments 8 to 11, known to those skilled in the art, which monitor the conditions in the tank and actuate the electronic control actuators when transfers are made and when other actions are taken. The regulatory safety valve 7 prevents unexpected and accidental overpressures and the heating element 6 (which may be placed [[sic]] on the outside, between the insulation, by heating coils conveying a warm liquid [lime]) keeps the temperature constant inside the tank.

The liquid is sent via the line 12, fitted with a pump, into the reactor 13 and the waste, cut up in the cropper 14, advantageously a guillotine, is sent by the chain conveyor 15 into the reactor 13, the solid materials must be immersed, the amount of caustic liquid is attained by the operation and control of a probe which also actuates the closure of the valve 17 and the start of the stirring provided by the mixer 16. The temperature of the reactor is maintained by the heating system 18. After approximately 30 minutes treatment at 350°C, the materials are deconsolidated, the caustic liquid is extracted by the line 19, fitted with a pump, through a filter 21, to the buffer tank 20. The filter 21 retains the particles greater than 1 mm. It is unclogged

suddenly by closing the valve of the line 19 and sending compressed air 44 into that part of the line [18] 19 [[sic]] which is connected to the tank 13.--.

Replacement for the third paragraph at page 8, line 15 - page 9, line 4:

--As this is a heat treatment, it is preferable to work continuously as long as possible. For this purpose, and in order to avoid shut downs due to the build-up of impurities and small particles, cleaning devices are provided for removing them, without having to stop the production. After a number of treatments and in anticipation of cleaning the buffer tank 20, the NaOH liquid in the master tank 5 will be taken to the minimum level in order to receive the entire solution stored in the buffer tank 20, up to the level of the tap on the line 21. Next, water will be slowly added via the line 37 to the rest of NaOH liquid, bottom of the buffer tank 20 for a direct dilution to the point of non-crystallization (concentration +/- 40%). After this dilution, the valve 38 is opened on a vibrating screen 39 having a porosity of 10 microns. The solid particles are removed to a container 40 and will be able to be transferred thereafter to a washing tank external to the system with a filter press for the impurities precipitated by the neutralization and for recovering the materials to be recycled in a [containers [sic]] container of the 36 type. The 40% NaOH solution is recovered via the outlet 41. It will be put into drums and sold for another use or else introduced into the tank 24 in order to obtain a neutralizing agent and thus increase the profitability of the process.--.

Replacement for the third full paragraph at page 9, lines 20-27:

--During temporary shut-down or shut-down of short [of] duration [[sic]] of the plant, the heating of the master tank 5 and possibly buffer tank must not be cut off. For a complete shut-down, it will be essential to drain, while hot, the buffer tank 20 to the master tank 5 and then via the line 43, connected to a battery of drums in which the solution will crystallize. To reuse the NaOH, the drums will be placed in the oven 1.--.

PROCESS AND PLANT FOR SEPARATING THE CONSTITUENTS OF WORN TYRES

The present invention relates to a process and a plant for the treatment of vulcanized rubber of all kinds, such as tyres, conveyor belts, boots, shoes and other objects containing assembled rubber and polymer materials for the purpose of recycling the component [sic] by the relevant industries.

The bulk of these materials is represented above all by the increase in road transport development which gives rise to worrysome quantities of downgraded tyres difficult to remove and possibly to recycle.

It should not be forgotten that more than 3 billion tyres, merely from private vehicles, are running along the roads in the various countries and, of course, have to be periodically replaced. In terms of weight, this represents at least 18 million tonnes of bulky waste which has to be disposed of, something which represents a serious ecological problem difficult to solve, and above all since people are becoming increasingly aware of environmental problems and regulations.

A vast quantity of tyres is destroyed by incineration and in cement kilns with recovery of thermal energy. This approach is being increasingly questioned because of the atmospheric pollution and of the destruction of materials which are beneficial to recover.

Another process consists of successive grinding so as to end up with small particles that can be used as fillers in bitumens and asphalts. Such grinding has been facilitated by cryogenic techniques. However, multiple shredders, which are indispensable for shearing the metal reinforcements, in order to produce reusable powder, are heavy machines which devour energy and are consequently very expensive.

Another destruction process, with recovery of certain components, is based on pyrolysis. The recycling consists in recovering the pyrolysis oil, the carbon and the metals. These processes are high-performance processes but they require the investment of large sums of money and high treatment costs, they are often the source of significant atmospheric pollution.

Thus efforts have been intensified to develop methods for stripping this bulky waste in a manner which is effective, economical and environmentally non-polluting. Considerable research has been focused on the problem, which obviously does not concern only worn tyres but all manufactured products made of rubber and also the waste accompanying the manufacture of these products, these often being reinforced with metal reinforcements or reinforcements made of synthetic materials. The ultimate problem does not reside only in the economical destruction of the rubber element or of the tyres, but it is also desirable to be able to recover and reuse them, or some of the components, for the purpose of avoiding unnecessary wastage of beneficial materials.

With the aim of illustrating the prior art in this field, it is appropriate to mention the following publications:

- GB 2,026,144 (1979) of writing [sic] a plant for the treatment of rubber waste and of synthetic materials coming from worn tyres. Thermal decomposition of the product, which is coarsely reduced, is carried out in a fluidized bed of sand at 800°C in the presence of oxygen. The gases produced by the decomposition are used and, at the end of the process, the reinforcing metals are recovered by means of magnets.

- US 4,426,459 (prior. JP 1980) discloses a process for the decomposition of vulcanized rubber by a treatment

around 100°C with an organic solvent in the presence of an alkaline hydroxide such as potassium hydroxide.

- DE 3,313,470 (1983) relates to a method and to an apparatus for treatment at a temperature above 200°C for 10 to 35 minutes in a liquid phase composed of spent mineral oils and of organic solvents. A viscous product is obtained which can be used as an additive in bitumens or insulation layers.

- WO 97/1561 (prior. US 1995 and 1996) describes a process for the devulcanization of rubber coming from downgraded tyres by desulphurization at around 300°C by means of an alkali metal in a medium that does not contain oxygen, before or during a treatment by an organic solvent after having separated the constituents of the tyres, such as the steel and other reinforcements.

Many of these processes have disadvantages, namely from the standpoint of the investments, of the efficiency, of the complexity, of the environment or of the market.

The object of the present invention is to remedy these drawbacks and to propose a process and a simple plant allowing separation of vulcanized and/or bonded rubber waste, such as tyres, belts or other objects, and allowing the constituents to be recovered for reuse by industry, without endangering the environment. The separation of the rubbers from the other materials and metal or other reinforcements is easily accomplished, quickly and economically, the reinforcements made of synthetic resins being dissolved and the metal recovered. Thus, it is possible to provide industry with quality products at competitive prices.

The process essentially comprises the following steps:

A) The reinforced or non-reinforced, vulcanized- rubber waste is coarsely reduced by cutting it up by means of a saw, preferably of the guillotine type fitted

with cutters in a grating in order to obtain fragments 10 to 25 cm in length. The sole purpose of this is to reduce the size and thus facilitate handling during the treatment process.

B) The reduced waste is introduced into a reactor and treated for 30 minutes at 350°C with an OH^- ion generator, preferably a strong alkaline base such as molten NaOH. 3.[sic] Separation of the basic liquid and the residues coming from the treated rubber.

C) Neutralization of the residues with an acid, such as phosphoric acid;

D) Recovery and separation of the rubber constituents and the metals used for reinforcement.

Destruction of some of the bonds between the rubber and the other reinforcing materials is achieved by the action of a strong alkaline base, such as molten NaOH which is maintained at a temperature of 350°C for approximately 30 minutes.

It is important to point out that the consumption of basic agent is very low and the etching liquid can be reused several times, by recovery and reinjection; the volume of the NaOH liquid product circulating will be automatically readjusted if necessary by a fresh addition of the product. Moreover, it should be emphasized that the process according to the present invention does not involve any organic solvent. In addition, it works with waste which is only coarsely cut up and the substances serving for the proposed treatment are well known, commonly employed and inexpensive.

The plant for implementing the process is relatively simple and does not entail inordinate investment.

The details of the process according to the present invention will emerge from the description of the

plant which relates thereto, the description being given by way of non-limiting example.

- Figure 1 shows schematically the overall plant;
- Figure 2 shows, on a larger scale, the first part of one of the possible embodiments of the plant;
- Figure 3 shows, on a larger scale, the second part of one of the possible embodiments of the plant.

As shown in Figure 1, crystallized NaOH in its original package is melted in the oven 1, at a temperature of 300 to 400°C, before being introduced into the master tank 5, which is provided with a heater and in which the NaOH is maintained at a temperature of 380°C before being transferred to the reactor 13 into which the waste coming from the cropper 14 is also introduced. After 30 minutes of immersion and with stirring at the start of obtaining a temperature of 350°C [sic]. The liquid is conducted by the line 19, furnishes of [sic] a pump, to the buffer tank 20 and then sent to the master tank 5. The buffer tank is heated to a temperature of 380°C in order to prevent heat shocks occurring in the tank 5. Moreover, the buffer tank is designed to gather the precipitates and is organized for the separation and extraction of the small particles. The decomposition products from the reactor 13 are transferred to the neutralization tank 23 and, at the end of the treatment, the residues are transported to the magnetic sorting device 32 where the metals are separated from the polymers resulting from the treatment.

According to this embodiment illustrated in greater detail in Figures 2 and 3, a drum 0 containing crystallized NaOH is introduced into the oven 1, which matches the shape of the drum, in which oven the NaOH is heated to a temperature of at least 380°C. The upper part and the straight vertical part of the oven form a cover which opens about the spindle 2 fastened to the bottom right of the oven in order to allow the drum to be easily

loaded. A connection tube running to the pump 3 is introduced and connected to the bung of the drum.

The liquified NaOH is transferred to the master tank 5 in which it is maintained at 350°C.

The master tank 5 is equipped with conventional monitoring and control instruments 8 to 11, known to those skilled in the art, which monitor the conditions in the tank and actuate the electronic control actuators when transfers are made and when other actions are taken. The regulatory safety valve 7 prevents unexpected and accidental overpressures and the heating element 6 (may be placed [sic] on the outside, between the insulation, by heating coils conveying a liquid lime) keeps the temperature constant inside the tank.

The liquid is sent via the line 12, fitted with a pump, into the reactor 13 and the waste, cut up in the cropper 14, advantageously a guillotine, is sent by the chain conveyor 15 into the reactor 13, the solid materials must be immersed, the amount of caustic liquid is attained by the operation and control of a probe which also actuates the closure of the valve 17 and the start of the stirring provided by the mixer 16. The temperature of the reactor is maintained by the heating system 18. After approximately 30 minutes treatment at 350°C, the materials are deconsolidated, the caustic liquid is extracted by the line 19, fitted with a pump, through a filter 21, to the buffer tank 20. The filter 21 retains the particles greater than 1 mm. It is unclogged suddenly by closing the valve of the line 19 and sending compressed air 44 into that part of the line 18 [sic] which is connected to the tank 13.

The buffer tank 20 is equipped with the same monitoring, control and heating apparatuses as the tank 5; it has a configuration which allows settling and reheating of the caustic liquid to the temperature of 350°C in order

to avoid thermal shocks and the risk of crystallization in the master tank 5. The liquid in the decanted part and at the correct temperature in the buffer tank 20 is then sent back via the line 21, by gravity, slowly into the master tank 5.

When all the caustic liquid has been withdrawn from the reactor 13, the large valve 22 is opened and releases, by gravity, the materials in the reactor 13 into the neutralizing tank 23.

The neutralizing liquids for the above treatments and for cleaning the plant, coming from the tank 24, are conveyed by the line 25, fitted with a pump, to the neutralizing tank 23 into which the liquid is injected by sprayheads. The phosphoric acid coming from the tank 26 passes via the mixing unit 27 through the line 25. The materials and the liquid are vigorously stirred. The pH meter 11 sets the pH = 7 after a little more stirring, there is a hold period in order to allow the suspended materials to precipitate, the neutralized liquid is extracted just at the point of connection of the line 28, fitted with a pump, to the tank 23. Injections of air 44 into this line have the purpose of clogging the filter installed at the end of the line 28.

The neutralized liquid having been withdrawn, the large valve 29 is opened while the valve 30 remains closed. The neutralized liquid is found in the tube with the materials between the two valves 29 and 30, it is withdrawn through the bypass of the line 28, the bypass also being equipped at the end of the line with a filter unclogged by sudden injections of air 44, and then the liquid is directed into the tank 24. After removing the rest of the liquid, the valve 30 is gradually opened so as to release the solid material coming from the neutralizing tank 23.

The material is transported by a conveyor belt to the magnetic pulley 32 located at the end of the belt. The metals 33 are precipitated into the container 34 and the non-magnetic materials 35 end up in the container 36. The container 36 is provided with a double bottom, the material being deposited on the first bottom provided with a stainless steel filter whose porosity is less than 10 microns. The material is dried by liquid flow via a lateral pipe 45. The containers 34 and 36 are superposable and have opening bottoms.

Liquified NaOH has a boiling point greater than 1000°C; there is no pressure formation in the plant, however the equipment is designed to withstand a pressure of 10 bar in anticipation of possible heat shocks.

As this is a heat treatment, it is preferable to work continuously as long as possible. For this purpose, and in order to avoid shut downs due to the build-up of impurities and small particles, cleaning devices are provided for removing them, without having to stop the production. After a number of treatments and in anticipation of cleaning the buffer tank 20, the NaOH liquid in the master tank 5 will be taken to the minimum level in order to receive the entire solution stored in the buffer tank 20, up to the level of the tap on the line 21. Next, water will be slowly added via the line 37 to the rest of NaOH liquid, bottom of the buffer tank 20 for a direct dilution to the point of non-crystallization (concentration +/- 40%). After this dilution, the valve 38 is opened on a vibrating screen 39 having a porosity of 10 microns. The solid particles are removed to a container 40 and will be able to be transferred thereafter to a washing tank external to the system with a filter press for the impurities precipitated by the neutralization and for recovering the materials to be recycled in a containers [sic] of the 36 type. The 40% NaOH solution is recovered

via the outlet 41. It will be put into drums and sold for another use or else introduced into the tank 24 in order to obtain a neutralizing agent and thus increase the profitability of the process.

Cleaning during production of the storage tank 24 is also provided. This tank having fed the neutralizing tank 23, the surplus neutral liquid will be withdrawn up to the level of the tap of the line 42 in order to be put on standby in the neutralizing tank 23. This will be organized during the time for a treatment of the reactor 13 and for the neutralization which occupies the liquid. Provision shall be made for the tank 24 to be cleaned and for the liquid in the tank 23 to be returned to 24 during this reaction and neutralizing time

When the lower level corresponding to the tap of the outlet 42 is reached, the valve 43 opens and releases the particle-laden neutral liquid onto a vibrating screen identical to 39. The liquid is removed and the particles recovered.

During temporary shut-down or of short of duration [sic] of the plant, the heating of the master tank 5 and possibly buffer tank must not be cut off. For a complete shut-down, it will be essential to drain, while hot, the buffer tank 20 to the master tank 5 and then via the line 43, connected to a battery of drums in which the solution will crystallize. To reuse the NaOH, the drums will be placed in the oven 1.

For the neutralization, the process makes use of acids, preferably phosphoric acids for the neutralization. It is quite conceivable to use materials such as phosphoric acid solutions regarded as waste in the industry - this waste is available in large quantity. The process accepts various concentrations, even low concentrations, the adjustment is done automatically. Consequently, the system may be regarded as a

neutralization centre for these acids, constituting an appreciable financial plus, thus reducing the cost of the main treatment forming the subject of the present invention.

The recovered metals will be sent to the steel industry.

The other materials recovered from the tyres are friable and are converted into a fine powder with slight pressure. Devulcanization is not complete but the breaking of certain bonds is ensured. The friable nature and the polymeric composition of the residue make thereof a beneficial filler material, to be recycled in the manufacture of tyres and rubber articles, and for other non-limiting applications, such as in bitumens or other bitumenous mixes.

It is obvious that the present invention is in no way limited to the embodiment as described in the illustrative embodiment shown in Figures 1, 2 and 3. Variants may be made to it without thereby departing from the scope of the claims.

CLAIMS

1. Process for treating vulcanized rubber waste, particularly comprising tyres of all sizes and of all types and/or of other worn reinforced-rubber articles such as boots, inflatable boats; this process comprises:

- cutting the materials, particularly the tyres, into fragments from 10 to 25 cm in length;
- attacking, using a molten pure base, the tyres and other vulcanized articles made of rubber and/or polymers, in which base deconsolidation takes place;
- separting the molten base from the deconsolidated solid components;
- neutralizing the deconsolidated fragments;
- separating the liquid from the deconsolidated fragments;
- separating the metallic and synthetic deconsolidated fragments for the purpose of recycling or of reutilization.

2. Process according to Claim 1, characterized by the use of molten pure cast NaOH as the attacking liquid.

3. Process according to either of Claims 1 and 2, characterized in that the said separation comprises sedimentation of the deconsolidated fragments, separated beforehand from the molten base, in a settling and neutralizing liquid, and, after removal of the settling and neutralizing liquid, recovery of the deconsolidated fragments.

4. Process according to any one of Claims 1 to 3, characterized in that it includes recycling the liquid coming from the NaOH.

5. Process according to any one of Claims 1 to 4, characterized in that the molten NaOH treatment temperature is at least 400°C advantageously and preferably 350°C.

6. Process according to any one of Claims 1 to 5, characterized in that the molten NaOH solution is used well below its boiling point.

7. Process according to any one of Claims 1 to 6, characterized in that the deconsolidation treatment takes place in a closed reactor, the materials to be treated completely immersed.

8. Process according to any one of Claims 1 to 7, characterized in that the neutralization uses dilute acids, preferably phosphoric acid, more advantageously waste from certain phosphoric acid solutions.

9. Plant for implementing the process for treating vulcanized rubber, such as tyres, according to any one of Claims 1 to 8, characterized in that it comprises:

- a completely closed system with no atmospheric pollution;
- a device (1) for melting the NaOH in its packaging;
- a reactor (13) into which the waste, consisting of tyres cut into lengths of 10 to 25 cm, and a basic liquid are introduced so as to form an attack medium in which the synthetic materials are deconsolidated from the reinforcements;
- a separating device (19, 20, 21) allowing the attacking liquid to be separated from the deconsolidated fragments;
- a source (24, 25, 26) of neutralizing agent allowing neutralization of the deconsolidated fragments before they are recycled and reutilized;

- a device for the separation of metal neutralized fragments and polymer.

10. Plant according to Claim 9, characterized in that the reactor (13) has closable inlet and outlet openings (17 and 22), stirring equipment (16) and in that the said separating device comprises a filter (21), if necessary unclogged by the compressed-air device (44), capable of retaining inside the reactor the particles greater than 1 mm.

11. Plant according to either of Claims 9 and 10, characterized in that the neutralizing device comprises a tank (23) provided with an inlet communicating with the outlet (22) of the reactor, and with an outlet, the inlet and outlet being closeable, stirring equipment (16) and a filter if necessary unclogged by the compressed-air device in the output line with extension (28), spraying equipment for facility the neutralizing via the line (27).

12. Plant according to one or other Claim 9 to 11, characterized in that the neutralizing device comprises a tank (24) for injection of neutralized liquid and for recovery via the lines (25 and 28).

13. Plant according to one or the other Claim 9 to 12, characterized in that the neutralizing device comprises another tank, source of financial returns by the use of acid waste (26), connected to a mixing unit (27), on the line (25).

14. Plant according to one of the other Claim 9 to 13, characterized in that the devices for cleaning the precipitates and small particles, during treatment, are characterized by the equipment (38, 39, 40, 41, 42, 43).

15. Plant according to one or the other Claim 9 to 14, characterized in that a device (31) for transporting

the deconsolidated materials comprises magnetic separation of the metallic materials (32), possibly combined with an eddy-current system for the non-ferrous materials.

16. Process and plant according to one or the other Claim of 1 to 15, allowing recycling of the synthetic materials coming from worn tyres, with a pulverulent appearance, having polymeric characteristics propitious to recycling, into the starting material, the tyres. Other advantageous and non-limiting uses ought to appear.

ABSTRACT

The invention concerns a method for treating tyres, belts, inflatable boats, boots and other manufactured articles containing rubber, polymers and reinforcing elements, which is a close circuit system consisting in immersing the waste materials to be treated in a hot alkaline hydroxide bath, followed by neutralization of the resulting materials with a weak mineral acid solution for industrial re-use of said materials.

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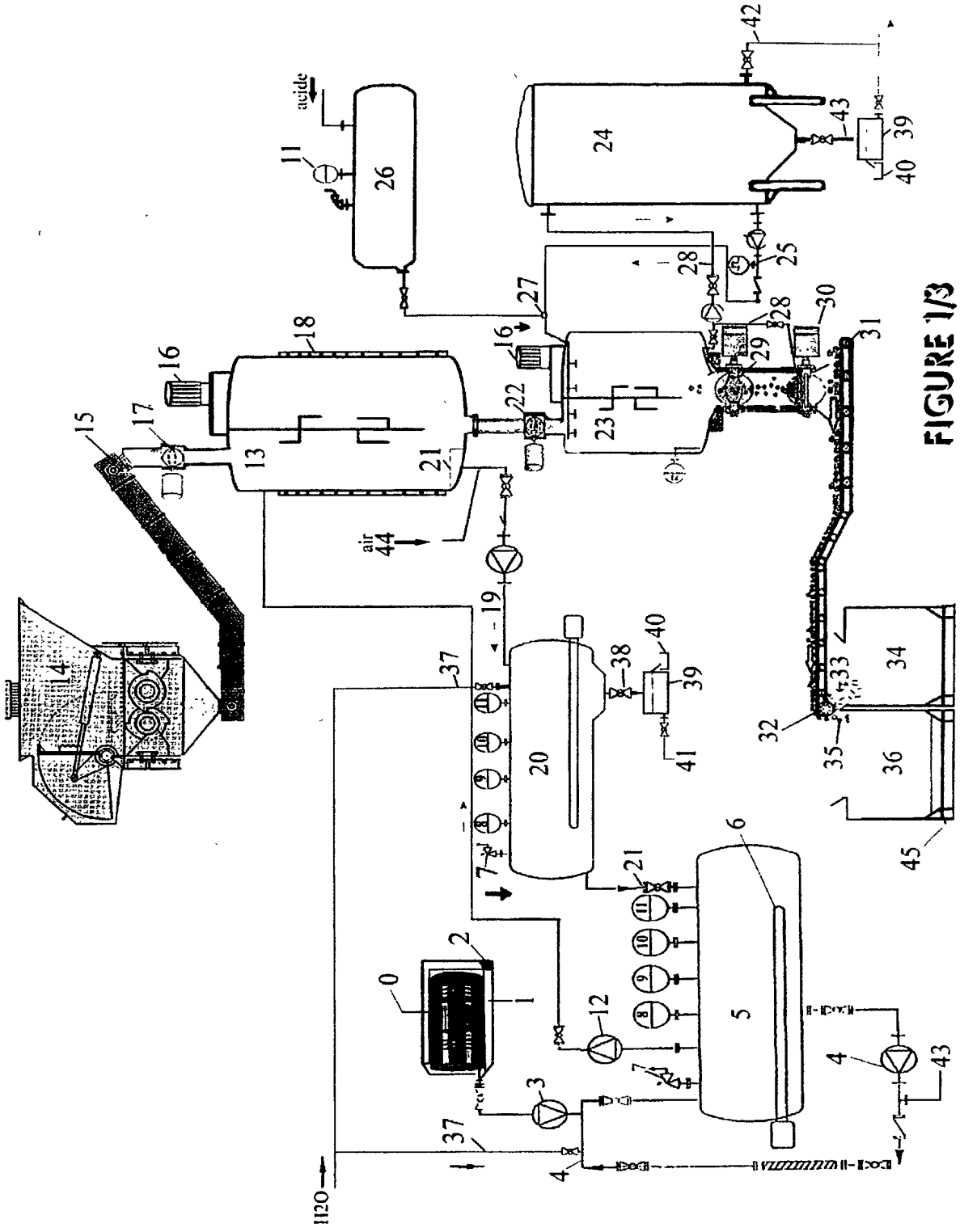

FIGURE 1/3

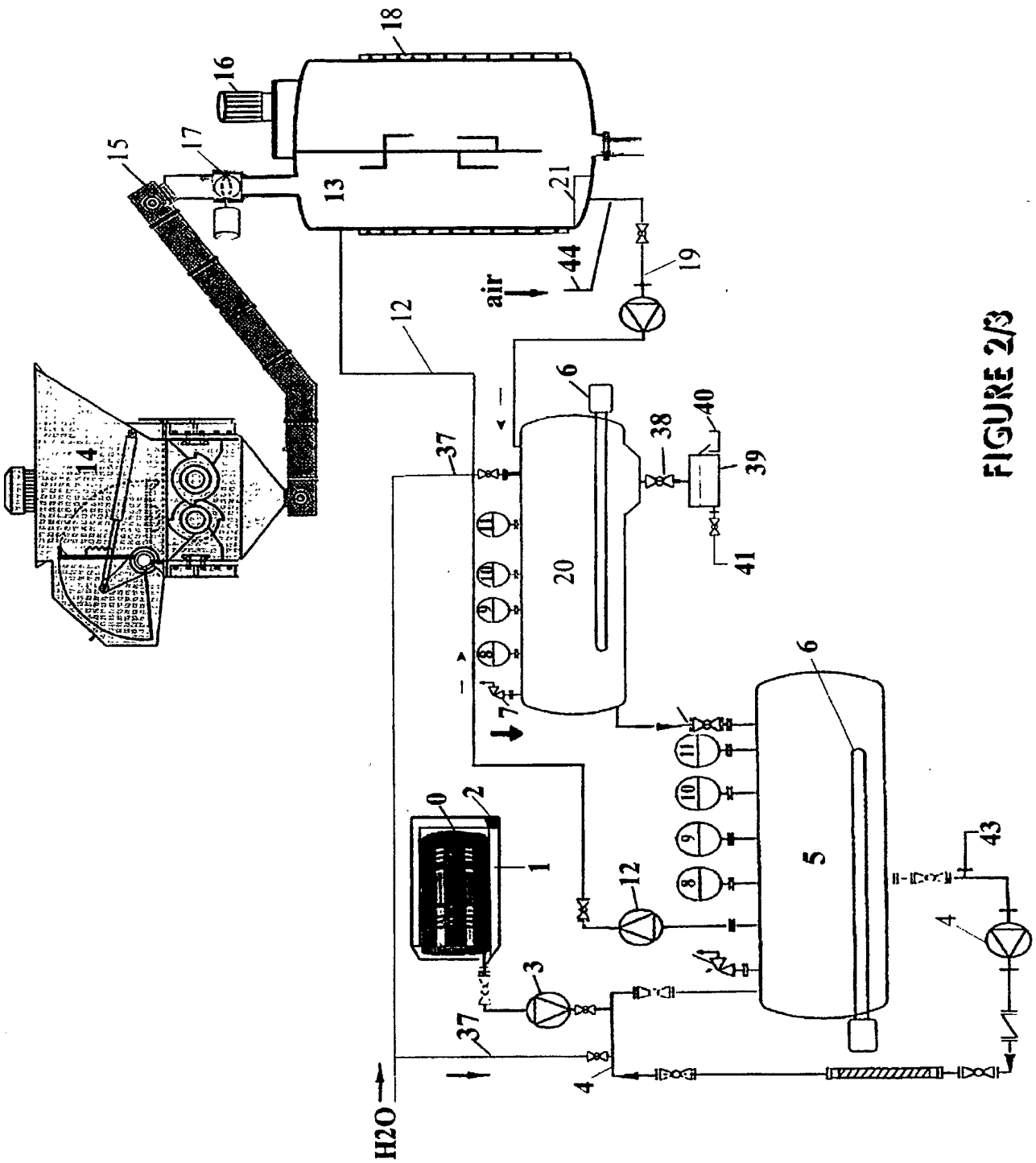

FIGURE 2/3

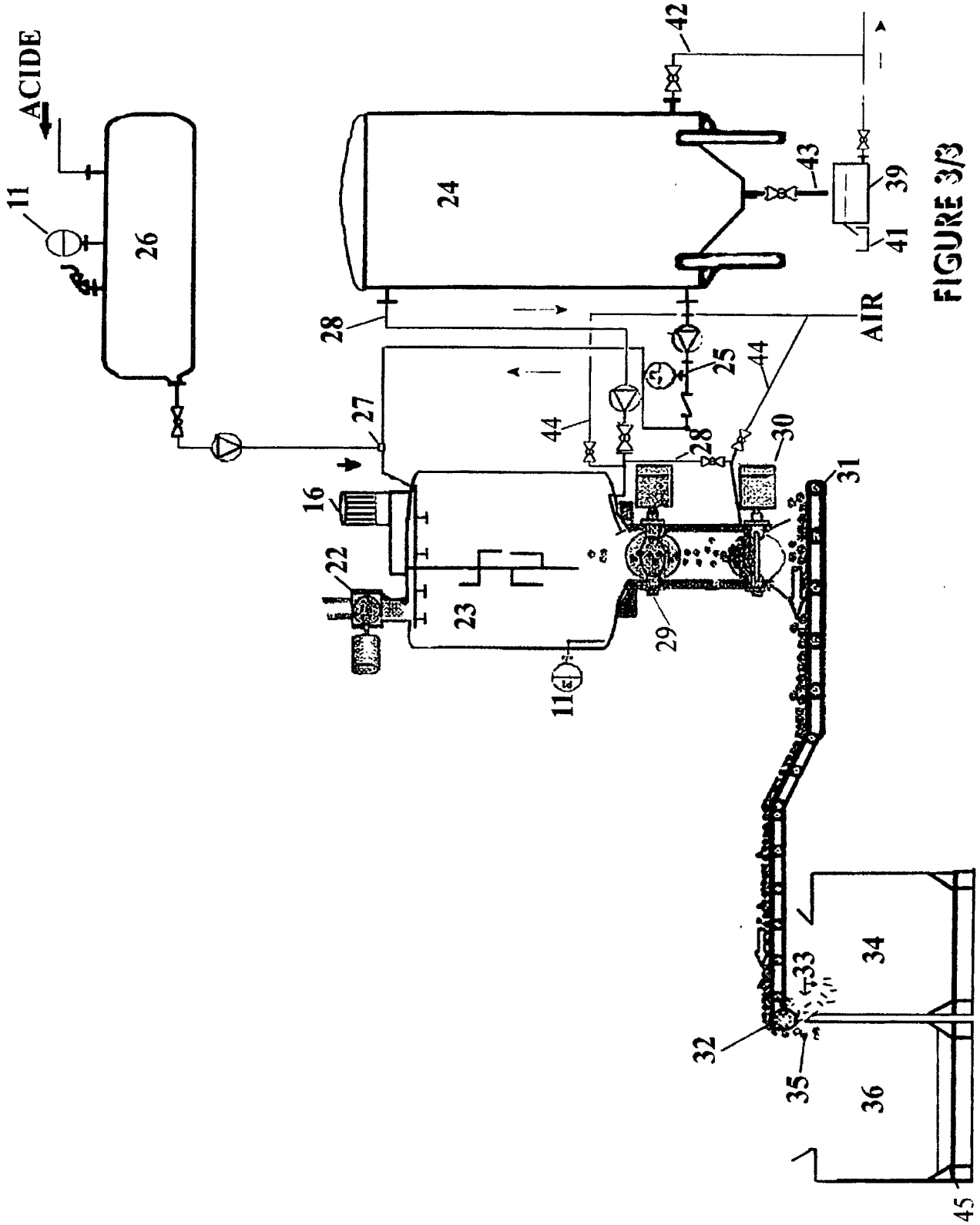

FIGURE 3/3

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	
First Named Inventor	DEBAILLEUL Gérard
COMPLETE IF KNOWN	
Application Number	/
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Process and plant for separating the constituents of worn tyres

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) [ ] as United States Application Number or PCT International Application Number [PCT/BE98/00180] and was amended on (MM/DD/YYYY) [11/20/1998] (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	NO
9700933	Belgium	11/20/1997	☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	
		☐ Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

DECLARATION — Utility or Design Patent Application

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s), or 365(c) of any PCT International application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application or PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(If applicable)*

☐ Additional U.S. or PCT International application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: ☐ Customer Number [ ] → *Place Customer Number Bar Code Label here*
OR
☐ Registered practitioner(s) name/registration number listed below

Name	Registration Number	Name	Registration Number
Jerold I. Schneider	24,765		

☐ Additional registered practitioner(s) named on supplemental Registered Practitioner Information sheet PTO/SB/02C attached hereto.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])	Family Name or Surname
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☐ Additional inventors are being named on the ___ supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto